4

A NOTE ON THE TRANSFORMATION OF MANGANITE*

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(*Received, October* 10, 1963)

Plate II, III and IV

The transformation of manganite during heat treatment has been studied by x-ray diffraction using single crystals. It is observed that a single crystal of manganite transformed into a single crystal of pyrolusite (MnO_2) and then into a twinned crystal of Mn_2O_3 at 300°C and 500°C respectively. The rotation photographs of a single crystal of manganite, before and after heating, are shown in Plates II-IV. All these photographs show that there are definite oriented relationships between the original and transformed phases. The relationship between manganite and pyrolusite has been found as follows :

[100] Man	||	[100] Pyro
[010] Man	||	[010] Pyro
[001] Man	||	[001] Pyro

Assuming the structure of manganite as that proposed by Buerger (1936), it can be seen that the transformation of manganite to pyrolusite (rutile like structure) took place by the removal of H from OH ions present in the manganite structure. This process would reduce the axial parameters in the *a* and *c* directions of manganite by one half together with a contraction along the *b* direction. The possibility of removal of H from OH ions has been proposed by Bernal (1960) in the case of manganese oxyhydroxides where hydrogen can enter or leave a system when there is a corresponding valency change of the positive ions. Recently, Feitknecht and his co-workers (1960) have shown that when MnO_2 is reduced by N_2H_4, topochemical reactions take place by the migration of electrons and protons through the lattice without changing it much according to the following equation:

$$MnO_2 + ne^- + nH^+ = MnO_{2-n}(OH)_n$$

In that light the transformation of manganite to pyrolusite is just the reverse reaction.

* Locality :—Ilfeld, Herz, Germany (Indian Museum, Reg. No. P. 57).

The next reaction, i.e. the transformation of pyrolusite to Mn_2O_3, also shows orientational relationship. A careful examination of Plate IV reveal that along the zero layer line sharp spots due to the reflections from 200, 400, 600, 620, 640 and 800 planes occur on the powder diffraction lines. The occurrence of these spots on the zero layer line indicates that the rotation axis is parallel to one of the crystallographic axes of the cubic crystal. There are also streaky spots along the zero layer line due to reflections from (*hho*) and (*hhl*) planes. This is due to the fact that the rotation axis is also parallel to one of the [110] axes of the cubic crystal. Periodicities, corresponding to [100] and [110] directions, are also observed in the same photograph. Thus, like cryptomelane to Mn_2O_3 transformation (Fauling, Zwicker and Forgeng, 1960), the oriented relationship between pyrolusite and Mn_2O_3 can be written as

$$[100]_{Pyro} \;||\; [110] \quad \text{and} \quad [100]_{Mn_2O_3}$$
$$[010]_{Pyro} \;||\; [110] \quad \text{and} \quad [010]_{Mn_2O_3}$$
$$[001]_{Pyro} \;||\; [001]_{Mn_2O_3}$$

However, the complex nature of the Mn_2O_3 structure, with different orientations of the MnO_6 octahedra within it, stands in the way of understanding the mechanism of the transformation.

The work has been carried out in the Mineral Physics Section of the Central Petrological Laboratories of the Geological Survey of India. The author is very much grateful to Dr. M. V. N. Murty, Superintending Geologist, for his sincere encouragement during the progress of the work. His thanks are also due to all his colleagues for various helpful discussions.

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Indian Journal of Physics, Vol. XXXVIII, No. 1

PLATE—II

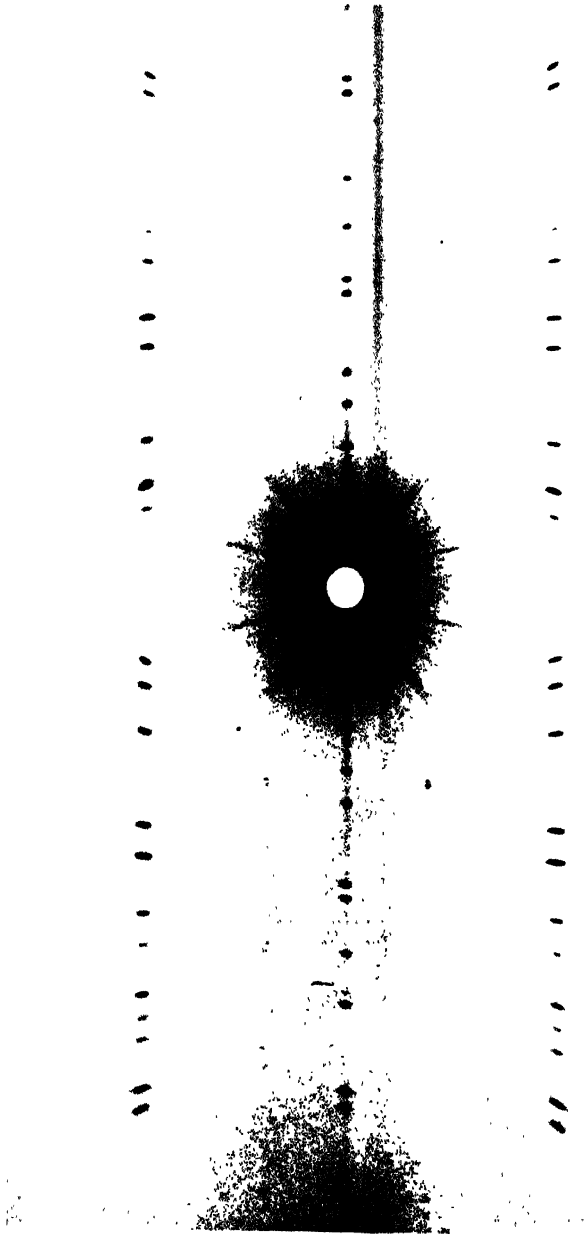

Fig. 1. X-ray rotation photograph of a single crystal of manganite taken along the 001 direction with Mn-filtered Fe-radiation. (Camera radius = 3 cms.)